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9917356.9

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1. Your reference

AROM-MET

2. Patent application number
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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

Cambridge University Technical Services
C/O The Old Schools
Trinity Lane
Cambridge CB2 1TS

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

7281587001

4. Title of the invention

AROMATIC MONOMERS AND POLYMERS FOR OPTOELECTRONIC DEVICES

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Professor A.B. Holmes
Melville Laboratory for Polymer Synthesis
Pembroke Street
CAMBRIDGE CB2 3RA

Patents ADP number *(if you know it)*

7035292009

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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Number of earlier application	Date of filing *(day / month / year)*

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Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature Andrew B. Holmes Date 22 July 1999

12. Name and daytime telephone number of person to contact in the United Kingdom

Professor A.B. Holmes
Tel 01223 334370
Fax 01223 334866

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AROMATIC MONOMERS AND POLYMERS FOR OPTOELECTRONIC DEVICES

The present invention is directed to conjugated molecules, oligomers and polymers for use in electric, electronic, optical and optoelectronic devices, e.g small molecule and polymer based light emitting devices such as light emitting diodes (LEDs). In particular the present invention concerns a process for the synthesis of aromatic precursors which when coupled together in controlled C-C bond forming processes afford luminescent conjugated molecules, oligomers, macromonomers and polymers.

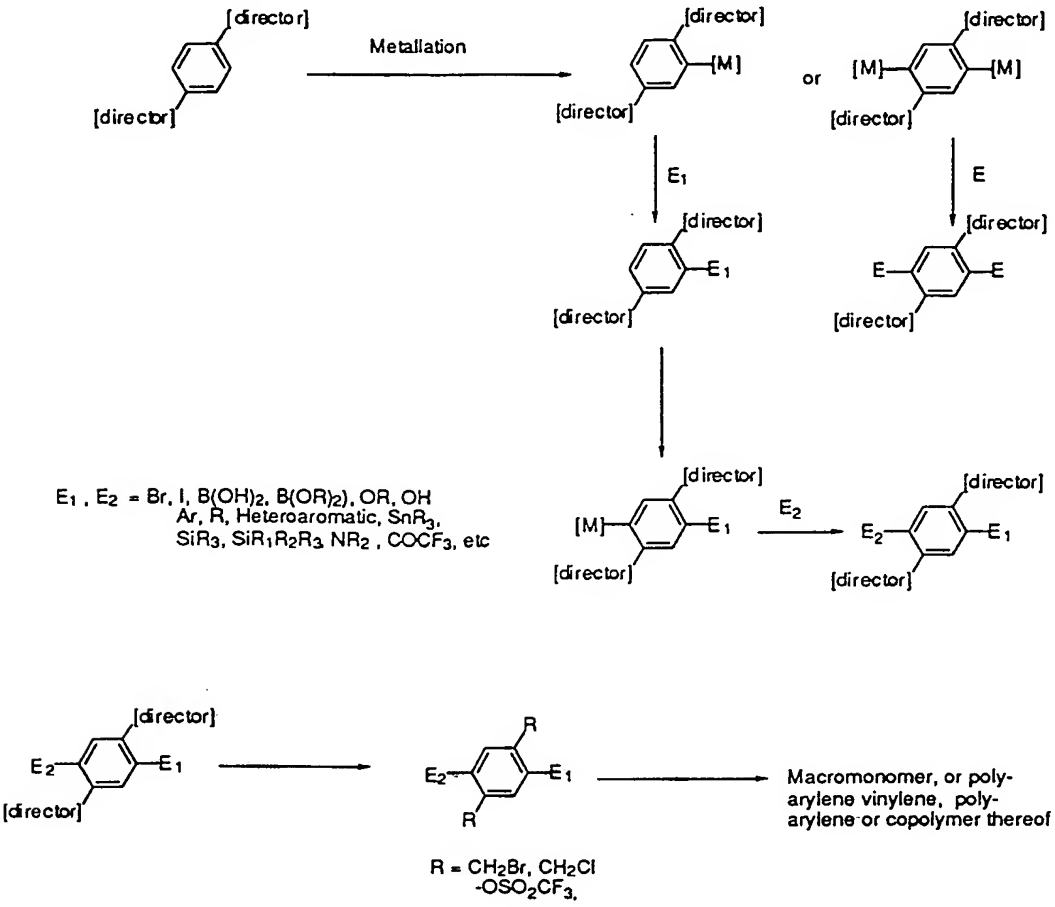
High photoluminescence efficiency in the solid state is an essential prerequisite for organic semiconductors capable of light emission through charge injection under an applied field (electroluminescence). Processes which deliver aromatic precursor molecules suitably disposed for coupling reactions are advantageous in the design of new conjugated systems for applications in luminescent devices. Much evidence is developing that variation of substitution patterns can afford improved efficiencies in photoluminescence.

Common procedures for coupling aromatic precursors to afford conjugated polymers for luminescent devices include (i) Gilch dehydrohalogenation polycondensation of 1,4-bis(halomethyl) aromatic derivatives (Gilch, *et al. J Poly Sci.* 1-A, 1966, **4**, 1337; Wudl, U.S. Pat. 5,189,136/1990). (ii) Suzuki (Pd catalysed)cross coupling of boronic acid derivatives with vinyl and aryl halides (Schlüter and Wegner, *Acta Polym.*, 1993, **44**, 59)
(iii) Horner Wittig polycondensation of bis(phosphonates) with dicarbonyl compounds (Kreuder *et al.*WO 96/10617 (1996); *Chem. Abstr.*, 1996, **124**, 345038u)
(iv) Nickel-catalysed cross coupling of aromatic dibromo-derivatives (Yamamoto, *Progr. Polym. Sci.*, 1992, **17**, 1153)
(v) McMurry coupling of dicarbonyl derivatives Feast, *et al.*, Abstracts of Papers of the American Chemical Society, 1998, Vol.215 (Pt2), pp.322-POLY; Daik *et al.*, *New J Chem.*, 1998, **22**, 1047).

The Gilch dehydrohalogenation method depends in particular on either radical bromination of the corresponding dimethyl derivative or halomethylation of a reactive precursor. The former suffers from low yields owing to electrophilic halogenation of the aromatic ring (especially when the other substituents are activating groups for electrophilic substitution) and the latter requires electron rich aromatic precursors for good yields in the halomethylation. The halomethylation is particularly unattractive for large scale manufacturing owing to the likely formation during the process of methyl halomethyl ether (halogen Cl or Br) which is a potent carcinogen. A process which would afford halomethyl precursors from alternative aromatic starting materials can deliver suitable substrates for Gilch dehydrohalogenation condensation, for phosphonate formation (leading to Horner-Wittig synthesis of conjugated oligomers

and polymers, and eventually carbonyl compounds for McMurry coupling.

In this invention is disclosed an efficient synthesis of substituted aromatic compounds for formation of oligomers, macromonomers and polymers.

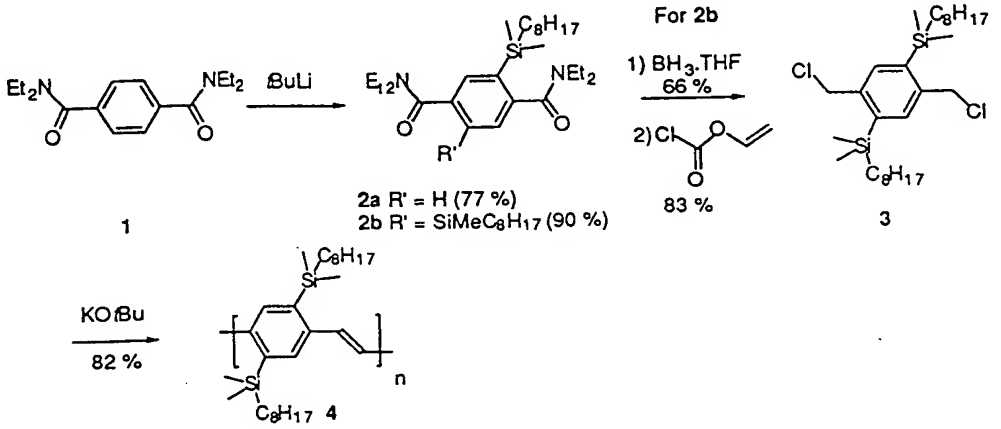


Analogous reactions can be envisaged for any heteroaromatic or aromatic starting material suitably functionalised with two "director" groups. Specifically the route could lead conveniently to substituted fluorene derivatives and naphthalene derivatives. The route is particularly attractive for functionalising aromatic molecules in a manner which is not easily reaisable by alternative synthetic strategies.

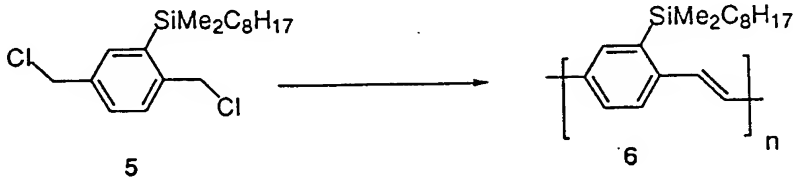
The directed metallation of bis-carbamates and urethanes has been reported (Snieckus Pure Appl. Chem., 1994, **66**, 2155; Bower *et al. J. Org Chem.*, 1998, **63**, 1514) and recognised as leading to precursors for the synthesis of organic natural products.

In a specific embodiment halomethyl precursors for Gilch dehydrohalogenation are prepared. This involves conversion of the "director" group into a halomethyl substituent through a number of chemical steps.

A worked example illustrates the metallation of the bis-amide **1** to yield either mono- or bis-metallated derivatives and eventually the mono- or bis-silylated precursors **2a,b**. These have in turn been polymerised to the corresponding conjugated polymers. The example shown is the bis-silyl polymer **4**. The analogous mono-silyl polymer has also been prepared. The advantage is the high yielding process for the synthesis of a precursor (e.g **3**) and that avoidance of the carcinogenic chloromethyl methyl ether.

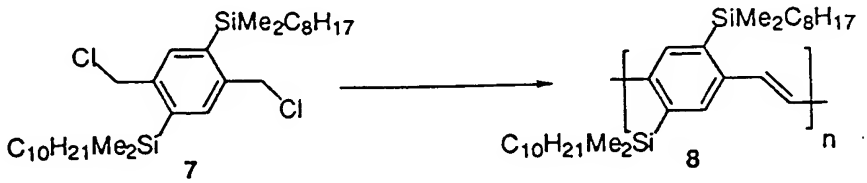


In another worked example monomer **2a** has been used to prepare monomer **5** leading to DMOS-PPV **6** [D.-H. Hwang, S.T. Kim, H.K. Shim, A.B. Holmes, S.C. Moratti and R.H. Friend, *Chem. Commun.*, 1996, 2241-2242] in good yield.



Asymmetric ring substitution of polyarylene vinylenes is expected to disrupt interchain packing and so lead to increased luminescence efficiencies [M. R. Andersson G.Yu, and A.J. Heeger, *Synth. Met.*, 1997, **85**, 1275].

The asymmetrically substituted aromatic precursor **7** has been prepared with surprising efficiency and converted into the highly luminescent unsymmetrically substituted PPV derivative **8**.

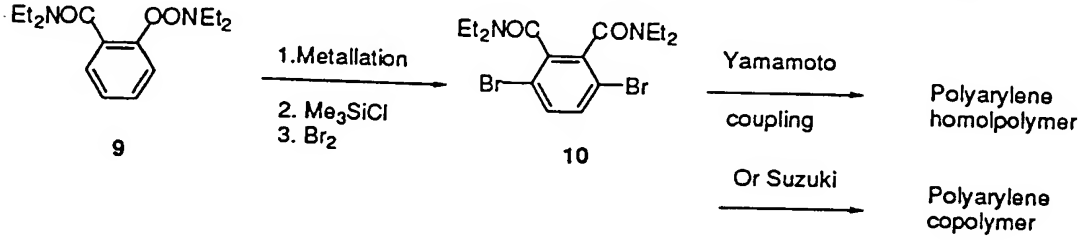


In principle any precursor analogue of **2a** or **2b** containing aryl (heteroaryl) or alkyl chains can be prepared by a C-C coupling reaction of the organo lithium derivative or other

metal derivative (stannane, boronic acid or ester, organocuprate, organozinc, organonickel etc). The advantage of the method is the potential control of the substituents which could be sequentially introduced and therefore different from one another. Another advantage is the surprisingly easy access to a wide variety of unsymmetrically substituted precursor molecules which can be incorporated into many different kinds of polymers.

N,N-diethylcarboxamide ($-CONEt_2$) and urethane substituents ($-OCONEt_2$) substituents are used to direct metallation with t-butyl lithium to adjacent positions. The resulting organo-lithium can be alkylated (silylated), boronated, stannylated and converted into a range of organometallic derivatives for new C-C bond formation to the aromatic ring. The resulting metal derivative can undergo transition metal catalysed cross coupling with a variety of other functional reagents to introduce new substituents or it could be cross coupled with suitable precursors in a polymerisation reaction.
The carboxamide group can be reduced to a tertiary amine and ultimately converted into CH_2Cl or CH_2Br for Gilch polymerisation. Urethane can be cleaved to phenol, converted into triflate and subjected to metal-mediated cross coupling to give poly(arylene)s, poly(arylene-vinylenes) by Heck reaction (for example) or poly(arylene ethynylenes) by Sonogashira polycondensation.

The process is extendable to any aromatic molecule which has directing substituents. Provided either the introduced substituents or the directing groups themselves can be modified into suitable substituents for cross coupling reactions mentioned in the above illustrative polymerisation procedures (i)-(v) the process offers a wide variety of novel substituted precursors for the synthesis of conjugated oligomers and polymers for luminescence.



The above worked examples illustrate processes for the synthesis of poly(2-dimethyloctylsilyl-1,4-phenylene-vinylene) and poly(2,5-bisdimethyloctylsilyl-1,4-phenylene)-vinylene as well as the unsymmetrical polymer **8**. These polymers exhibit a PL efficiency in excess of 60% in the solid state and can be fabricated as the emissive layer in polymer LEDs in which ITO (on glass) and Al are the metal contacts.

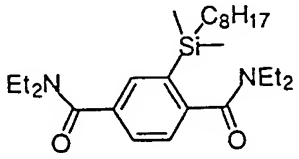
It is expected that many aromatic and heteroaromatic precursors could be prepared by the above directed metallation procedure. Boronate and halo-substituted

precursors for Suzuki cross coupling of substituted fluorene derivatives could be made in processes leading to novel conjugated materials. Preferably the process can be used for bis(halomethyl) precursors for Gilch dehydrohalogenation.

In another embodiment reaction of the metallated derivative with CF_3CO_2Et would lead to the corresponding mono- or bis trifluoroacetyl-substituted derivatives which through Horner polycondensation can yield novel CF_3-substituted poly(arylene vinylene derivatives).

Worked Example

2-Dimethyloctylsilyl-tetra-*N*-ethyl-terephthalamide



Tert-butyllithium (253 ml, 0.43 mmol) was added to tetra-*N*-ethyl-terephthalamide (100 mg, 0.36 mmol) in 30 ml of anhydrous tetrahydrofuran cooled with a bath of acetone-nitrogen. After 30', chlorodimethyloctylsilane (102 ml, 0.43 mmol) was added. The mixture was left to reach room temperature in its bath over three hours. Brine water was added and extracted with dichloromethane. The organic extract was dried with magnesium sulfate and concentrated *in vacuo*. Column chromatography using hexane / ethyl acetate (60 / 40) as an eluant (Rf = 0.54 ; hexane / ethyl acetate (85 / 25)) gave a white solid (Yield: 78 %).

Mp = 46 °C

IR (KBr) in cm^{-1}: 2972, 2926, 2854, 1623, 1484, 1430, 1383, 1291, 1251, 1220, 1105, 1062, 842.

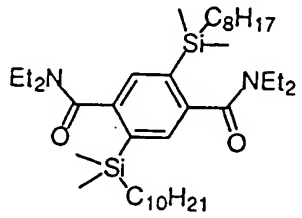
^{1}H-NMR δ_H ($CDCl_3$, 250 MHz) 7.40 (d, 1 H, J = 1.57 Hz), 7.22 (dd, 1 H, J_1 = 7.75 Hz, J_2 = 1.57 Hz), 7.09 (d, 1 H, J = 7.75 Hz), 3.45-3.36 (m, 4 H), 3.06-2.98 (m, 4H), 1.15-0.90 (m, 25 H), 0.74-0.64 (m, 4 H), 0.12 (s, 6 H).

^{13}C-NMR δ_C ($CDCl_3$, 62.5 MHz) 171.6, 171.0, 143.6, 137.4, 136.5, 132.8, 126.3, 125.6, 43.4, 38.9, 33.5, 31.8, 29.2, 29.1, 23.8, 22.5, 15.9, 14.0, 13.6, 12.7, -2.3.

MS: (CI) *m/z* 447.3400 (M^+) $C_{40}H_{80}N_2O_2Si$ requires *M* 446.7400.

found C: 69.99%, H: 10.22%, N: 6.27%
calc.: C: 69.90%, H: 10.39%, N: 6.27%

2-Dimethyloctylsilyl-5-dimethyldecylsilyl-tetra-*N*-ethyl-terephthalamide



At -78 °C, *sec*-butyllithium (2.9 ml, 3.7 mmol) was added to a solution of tetramethylethylenediamine (0.55 ml , 3.7 mmol) in 15 ml of dry tetrahydrofuran. 2-dimethyloctylsilyl-tetra-*N*-ethyl-terephthalamide (1.26 g, 2.8 mmol) in 15 ml of dry tetrahydrofuran was added dropwise and the mixture was stirred at -78 °C for 20'. After addition of chlorodimethyloctylsilane (1 ml, 3.7 mmol), the reaction was left to reach room temperature in its bath overnight. Brine water was added and extracted with dichloromethane. The organic extract was dried with magnesium sulfate and concentrated *in vacuo*. Column chromatography using hexane / ethyl acetate (80 / 20) as an eluent (Rf = 0.41; hexane / ethyl acetate (80 / 20)) gave a white solid (Yield: 85 %).

IR (KBr) in cm^{-1}: 2955, 2922, 2852, 1635, 1482, 1455, 1424, 1380, 1276, 1247, 1129, 1086, 868, 839, 813.

^{1}H-NMR δ_H($CDCl_3$, 250 MHz) 7.33 (s, 2H), 3.54 (q, 4H, J = 7.15 Hz), 3.12 (q, 4H, J = 7.15 Hz), 1.30-0.52 (m, 50 H), 0.21 (s, 12 H).

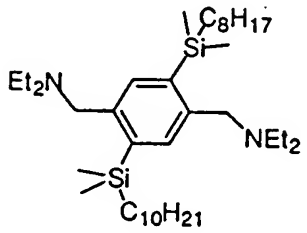
^{13}C-NMR δ_C($CDCl_3$, 62.5 MHz) 172.4, 142.2, 137.3, 132.2, 43.3, 38.9, 33.7, 31.9, 29.7, 29.4, 24.0, 22.7, 16.0, 14.1, 13.8, 12.8, -2.3.

MS: (CI) *m/z* = 644.5132.

Elemental analysis (645.17 for $C_{38}H_{72}N_2O_2Si$)
found C: 70.84%, H: 11.26%, N: 4.39%

calc.: C: 70.75%, H: 11.25%, N: 4.34%

2-Dimethyloctylsilyl-5-dimethyldecylsilyl-tetra-*N*-ethyl-p-xylylenediamine



To a stirred solution of 2-dimethyloctylsilyl-5-dimethyldecylsilyl-tetra-*N*-ethyl-terephthalamide (1.3 g, 2.3 mmol) in 30 ml of dry tetrahydrofuran was added borane-tetrahydrofuran complex (23 ml, 23 mmol). The reaction was refluxed for 18 h. Water was added carefully until the liberation of hydrogen stopped. The mixture was concentrated in vacuo and 6 N hydrochloric acid was added. The aqueous solution was heated at reflux for 4 h. The solution was cooled and adjusted to pH 9 with sodium hydroxide. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with magnesium sulfate and concentrated in vacuo. Column chromatography using hexane / ethyl acetate (96 / 4) as an eluent (Rf = 0.79; hexane / ethyl acetate (80 / 20)) gave a white solid (Yield: 52 %). Mp = 26 °C

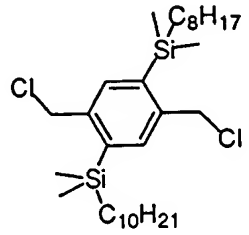
IR ($CHCl_3$) in cm^{-1}: 2963, 2922, 2852, 1466, 1370, 1248, 1203, 1166, 1121, 1057, 835.

^{1}H-NMR δ_H($CDCl_3$, 250 MHz) 7.71 (s, 2 H), 3.63 (s, 4 H), 2.51 (q, 8 H, J = 7.10 Hz), 1.30-0.81 (m, 50 H), 0.30 (s, 12 H).

^{13}C-NMR δ_C ($CDCl_3$, 62.5 MHz) 143.2, 137.821, 134.7, 58.6, 46.2, 33.7, 31.9, 29.7, 29.3, 24.2, 22.7, 16.6, 14.1, 11.7, -1.3.

MS: (MALDI) *m/z* 618.30 $(MH)^+$

2-Dimethyldecylsilyl-5-dimethyldecylsilyl-1,4-bis(chloromethyl)benzene



At 0 °C, vinyl chloroformate (70.3 ml, 82.7 mmol) was added to 2-dimethyldecylsilyl-5-dimethyldecylsilyl-tetra-*N*-ethyl-p-xylylenediamine (663 mg, 1.09 mmol) in 20 ml of dry dichloromethane. The mixture was stirred at room temperature for 5 h. Brine water was added and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried with magnesium sulfate and concentrated in vacuo. Column chromatography using hexane as an eluant (Rf = 0.46 ; hexane) gave a white solid (Yield: 65%). Mp = 40 °C

IR ($CHCl_3$) in cm^{-1}: 2923, 2854, 1466, 1411, 1377, 1344, 1254, 1192, 1172, 1140, 1108, 837, 792, 716.

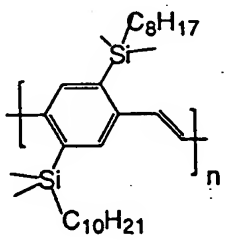
^1H-NMR δ_H ($CDCl_3$, 250 MHz) 7.57 (s, 2 H), 4.70 (s, 4 H), 1.36-1.29 (m, 29 H), 0.92-0.83 (m, 9 H), 0.42 (s, 12 H).

δ_C ($CDCl_3$, 62.5 MHz) 141.9, 140.2, 137.0, 46.5, 33.6, 32.0, 29.7, 29.6, 29.4, 29.3, 24.0, 22.7, 16.5, 14.1, -1.5.

found C: 66.52%, H: 10.31%

calc.: C: 66.38%, H: 10.41%

Poly [2-(dimethyloctylsilyl)-5-(dimethyldecylsilyl)-1,4-phenylene vinylene] **8**



To a degassed solution of 2-dimethyldecylsilyl-5-dimethyldecylsilyl-1,4-bis(chloromethyl)benzene (109mg,

0.2mmol) in 1.5ml of dry tetrahydrofuran was added a degassed solution of potassium-*tert*-butoxide (112.5mg, 1mmol) in 5ml of dry tetrahydrofuran over 10'. The mixture was stirred under nitrogen overnight. The solution was poured into methanol to give bright yellow flaks. The polymer was reprecipitated in acetone and dried overnight. (Yield: 26 %)

UV ($CHCl_3$) λ_{max}: 438 nm

UV (film) λ_{max}: 430 nm

Mn (GPC) 289000 ; Mw (GPC) 1065000 ; PD = 3.7

^{1}H-NMR ($CDCl_3$, 250 MHz) d/ppm vs.

TGA: decomposition at 350 °C.

DSC: decomposition at 300 °C. no Tg, no mp